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A Non-Hydrolytic Sol-Gel Approach for the Preparation of $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$ Powders

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Abstract. The study of non-hydrolytic reactions for the synthesis of $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$ solid solution with $x = 0.6$ is reported. The reagents chosen were $Al(OsBu)_3$, $Ti(OiPr)_4$, $TiCl_4$ and $Mg(NO_3)_2{\cdot}6H_2O$ in toluene. The reactions were followed using ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. Sol-gel synthesized powders were calcined in air at 300, 500, 1000, and 1200°C for 1 h. The powders were analysed by X-Ray Diffraction (XRD) demonstrating the formation of a $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$ phase in samples treated at the higher calcination temperature.

Keywords: $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$, non-hydrolytic sol-gel, NMR, precursor chemistry, solid solution

Introduction

Interest in aluminium titanate spans a wide range of technologies because of its unique thermal and chemical properties [1, 2]. Many studies have been reported on the synthesis of aluminium titanate derivatives [3–5]. Among them, a sol-gel method indicated the possibility to decrease processing temperatures and hence achieve more effective microstructural control [6]. In fact, as for many other heterometallic ceramics, the use of sol-gel synthesis has the great advantage to achieve homogeneous mixing of the precursors which then relates to material homogeneity. We have previously reported the sol-gel preparation of aluminium titanate thin films which showed the formation of the metastable β-Al_2TiO_5 phase at 700°C, well below the eutectoid temperature (1280°C) [7].

Beside its existence as a metastable phase at temperatures below 1280°C, another drawback limiting the use of Al_2TiO_5 powders is their low mechanical strength [8]. Improvements have been reported to occur if appropriate dopants, such as MgO, are added [5, 9–11]. To avoid synthetic problems due to the different hydrolysis rates of aluminium and titanium alkoxides, non-hydrolytic sol-gel routes based on direct condensation of the precursors in aprotic solvents, can be used [6, 12]. This paper reports the synthesis and characterization of magnesium doped aluminium titanate of composition $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$. The indicated composition was targeted for its reported high thermal stability [13, 14].

Experimental Procedure

All reagents (Aldrich) and solvent (Carlo Erba) were reagent grade and were used without further purification. The synthesis was carried out under N_2.

$Al(OsBu)_3$ (2.04 ml, 8 mmol) and $Ti(OiPr)_4$ (1.48 ml, 5 mmol) were carefully added to toluene (50 ml). The solution was stirred at room temperature for 10 min and then $TiCl_4$ (1.20 ml, 11 mmol) was quickly added. The resulting solution was refluxed under magnetic stirring for 2 h. The solution was cooled to room temperature, and then $Mg(NO_3)_2{\cdot}6H_2O$ (1.54 g, 6.0 mmol) was added. A yellow-orange precipitate rapidly formed. The mixture was stirred at reflux for 1 h, evaporated to dryness and dried for 12 hours at 110°C. Different portions of the yellow-orange precursor were directly placed in a preheated furnace and fired

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in air at temperatures of 300, 500, 1000, and 1200°C for 1 h.

Samples for NMR measurements were prepared directly in the NMR tube following the procedure described above scaling the amount of reagents in order to have a total volume of 3 ml. ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 100.56 MHz. Chemical shifts are given in ppm from tetramethylsilane (TMS) and referenced against solvent signals.

The thermal decomposition behaviour of the precursor was studied by simultaneous thermogravimetric and differential thermal analysis (TG/DTA, model STA 409, Netzsch), with a heating rate of 10°C/min in air.

The phases present in the powders calcined at the four different temperatures were analysed by X-Ray Diffraction analysis (XRD, model XPert Pro, Philips). XRD spectra were taken in the range $2\theta = 15 - 55^\circ$ with a scan step size of 0.03° and using graphite-filtered Cu K_α radiation (40 kV, 40 mA).

Results and Discussion

The non-hydrolytic synthetic procedure chosen was based on the condensation reaction between metal alkoxides and metal chlorides so that the by-products, volatile alkyl chlorides, could be easily eliminated. Magnesium was added in the final step of the synthesis as $Mg(NO_3)_2{\cdot}6H_2O$.

Toluene was chosen as solvent for its low polarity and low coordinating properties which make it an excellent solvent for most organometallic species.

The synthesis was monitored by means of ^{13}C NMR spectroscopy, a technique which was successfully used to study the preparation of Al_2TiO_5 thin films via a conventional sol-gel route [7]. Figure 1(a) shows the ^{13}C

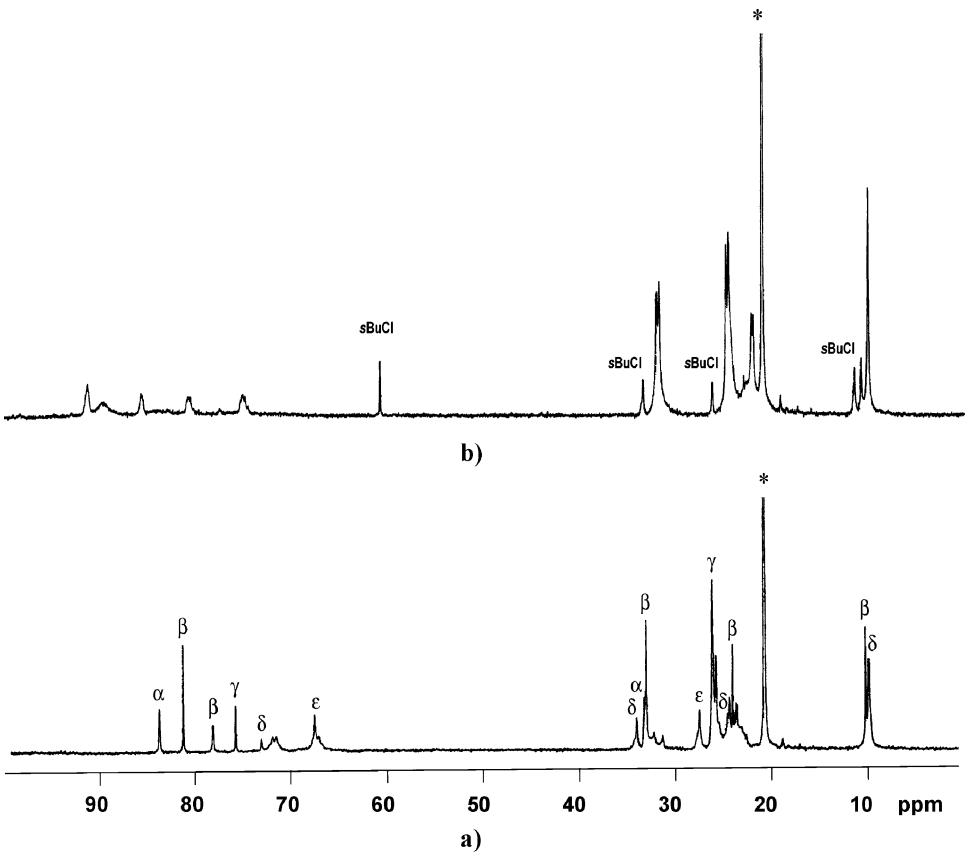

Figure 1. ^{13}C NMR spectrum of: (a) $Al(OBu^s)_3 + Ti(OPr^i)_4$ in toluene at room temperature. (b) $Al(OBu^s)_3 + Ti(OPr^i)_4 + TiCl_4$ in toluene after 2 h at reflux. α: $Ti(OBu^s)_4$, β: $Ti(OBu^s)_{4-x}(OPr^i)_x$, γ: $Ti(OPr^i)_4$, δ: $Al(OBu^s)_3$, ε: $Al(OPr^i)_3$. An asterisk marks the solvent signal. The assignment of signals α, β, γ, δ, ε were made by comparison with pure samples.

spectrum of the initial $Al(OsBu)_3$ and $Ti(OiPr)_4$ solution in toluene. The main reaction that took place at room temperature was the redistribution between the alkoxide groups bonded to titanium and aluminium, as witnessed by the appearance of the resonances due to $Al(OiPr)_3$, $Ti(OsBu)_4$ and $M(OsBu)_x(OiPr)_y$ species. Addition of $TiCl_4$ and reflux for 2 h resulted in significant spectral variations as shown in Fig. 1(b). The resonances at 60.4, 33.4, 25.0 and 11.1 ppm due to 2-chlorobutane, that appeared together with new broad peaks in the low field region of the spectrum, indicated the occurrence of condensation reactions. No presence of *i*PrCl was observed probably due to the volatility of the 2-chloropropane. The numerous resonances between 75 and 90 ppm showed the presence of different coordination environments for Al and Ti. However, the high values of the chemical shifts of the new peaks, probably due to chlorine atoms still present in the polymer network, indicated that the reaction was not complete.

When magnesium nitrate hexahydrate was added, to complete the preparation procedure, the formation of a precipitate was observed.

Figure 2 shows the thermal decomposition behaviour of the sol-gel synthesized precursor dried at 100°C for 2 h. The DTA curve shows two endothermic peaks with their maxima at around 200 and 230°C associated to a weight loss of about 40% as observed in the TG curve which can be ascribed to the loss of water and to decomposition reactions of residual organic moieties in the precursor. These reactions lead to carbonaceous residues, as evidenced by the black colour of powders fired at 300°C for 1 h. The endothermic transformations are followed by two overlapping exothermic peaks in the 250–600°C range associated to a further 10% weight loss attributable to the combustion of these residual carbonaceous components. Other DTA peaks at the temperature of about 950°C and above can be attributed to solid state phase transformations.

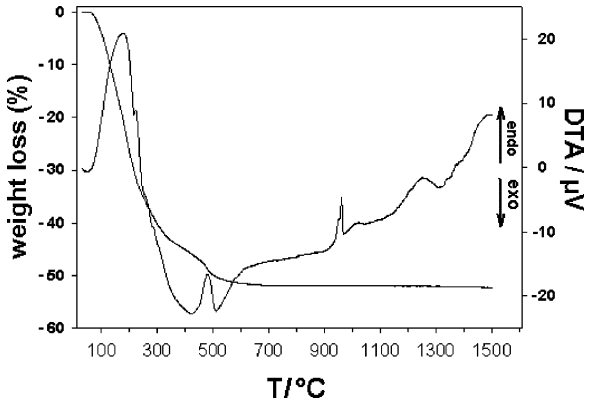

Figure 2. Simultaneous TG/DTA curves for the sol-gel synthesized precursor (10°C/min).

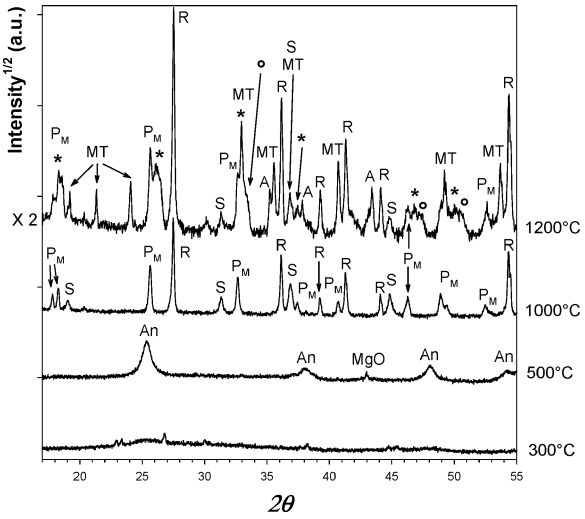

Figure 3. XRD spectra of the sol-gel precursor fired (1 h) in preheated furnace at different temperatures and quenched in air (An: anatase, R: rutile, P_M: $MgTi_2O_5$, S: $MgAl_2O_4$, MT: $MgTiO_3$, A: alumina, *: $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$, °: $Mg_{0.3}Al_{1.4}Ti_{1.3}$ or Al_2TiO_5).

Figure 3 shows the XRD patterns of the precursor fired for 1 h in a preheated furnace at 300, 500, 1000 and 1200°C. After calcination at 300°C, the powder was mostly amorphous. At 500°C, broad anatase peaks were present (JCPDS card no. 21-1272) and also the most intense peak of MgO phase (JCPDS card no. 45-0946) was detectable at $2\theta = 42.9°$. The XRD pattern of the powder fired at 1000°C showed the formation of $MgTi_2O_5$ phase (JCPDS card no. 35-0796), labelled P_M in the figure. Rutile (JCPDS card no. 21-1276) and spinel ($MgAl_2O_4$, JCPDS card no. 21-1152) were also clearly detectable.

The XRD spectrum of the powder fired at 1200°C was rather complex, given the presence of several crystalline phases with overlapping reflections. Besides $MgTi_2O_5$, rutile and spinel, which were already formed after 1 h treatment at 1000°C, the sample fired at 1200°C showed the presence of alumina (JCPDS card no. 78-2426) and magnesium titanium oxide ($MgTiO_3$, JCPDS card no. 79-0831). However, it is worth noting that $Mg_{0.6}Al_{0.8}Ti_{1.6}$ phase (whose peaks are indicated by an asterisk in Fig. 3) was also present. Indeed,

according to JCPDS card no. 34-1062, the (110) peak at 26.1°, the (040) peak at 37.4°, the (133) and (043) peaks at 46.8° and 46.9°, as well as the (200) and (025) peaks at 49.9° and 50.1°, respectively, clearly demonstrated the formation of the metastable $Mg_xAl_{2(1-x)}TiO_{(1+x)}$ solid solution with $x = 0.6$. Other peaks, labelled by an open circle in Fig. 3, could be attributed to either $Mg_{0.3}Al_{1.4}Ti_{1.3}$ (JCPDS card no. 33-0854) or Al_2TiO_5 (JCPDS card no. 70–1435).

Conclusions

Metastable $Mg_xAl_{2(1-x)}Ti_{1+x}O_5$ solid solution with $x = 0.6$ was obtained for the first time as a powder by 1 h calcination at 1200°C and subsequent air quenching of precursor prepared by non-hydrolytic sol-gel route. The lack of homogeneity, shown by XRD analysis, can be ascribed to the incomplete reaction that occurred in solution. Although the formation of $Mg_{0.6}Al_{0.8}Ti_{1.6}O_5$ was accompanied by other phases, these results indicate that $Mg_xAl_{2(1-x)}Ti_{1+x}O_5$ powders can be synthesized by sol-gel methods and suggest that phase purity of the solid solution can be improved by optimising reaction conditions (choice of reagents, concentrations, reaction times etc.) as well as thermal treatments.

Acknowledgments

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